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Absorption of Radium and Thorium From New Mexico Uranium Mill Tailing Solutions

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UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

	Page
Abstract	1
Introduction	1
Description of samples	2
Experimental procedures	4
Laboratory techniques	4
Analytical techniques	4
Experimental absorption studies	6
Supplemental absorption studies	7
Experimental desorption studies	8
Discussion, conclusions, and recommendations	8
References	10
Appendix.--Analytical procedures	11

ILLUSTRATION

1. Alpha spectrometer 5

TABLES

1. Composition of the New Mexico solid samples used in absorption tests 3
2. Radium, thorium, and uranium concentrations and pH values for New Mexico tailing pond solutions used in absorption tests 4
3. Removal efficiencies of radium and thorium using soils and tailing samples when contacted with tailing pond solutions 6
4. Radium removal efficiencies from tailing pond solutions by $BaCl_2$ additions 7
5. Desorption studies on 10 g of selected samples 8

ABSORPTION OF RADIUM AND THORIUM FROM NEW MEXICO URANIUM MILL TAILING SOLUTIONS

by

H. R. Beard,[1] H. B. Salisbury,[2] and M. B. Shirts[3]

ABSTRACT

The Bureau of Mines investigated the absorption of radium and thorium from waste uranium leach liquor by clays and other materials. This work was conducted in support of the Bureau's goal of minimizing the environmental conflicts, impacts, and occupational hazards associated with mining and milling operations. Tailing and soil samples from New Mexico were evaluated for their potential to absorb radium and thorium from tailing liquors. Absorption ranged from 0 to 97 pct for radium and 0 to 60 pct for thorium. Some samples that readily absorbed radium were contacted with various salt solutions that could be present in tailing solutions to determine whether desorption would be a potential problem. The desorption of radium ranged from 0 to 75 pct. An alpha spectrometric method was used to determine the radium and thorium concentrations in the solutions and solids.

INTRODUCTION

When uranium ore is processed, up to 5 pct of the radium is taken into solution. Most of this soluble radium passes through the uranium recovery operations to the tailing disposal system. Although the actual weight of radium and other soluble radionuclides is very small, the concentrations in the tailing pond solutions generally are far above the permissible levels. Only limited information is available on the distribution and disposal of radionuclides found in uranium milling operations. Most uranium plants use solar evaporation for disposal of excess processing water to prevent point discharge. Polyvinyl chloride-lined ponds are being used in some of the newest mills, but seepages from older operations are possible. A study of tailing solutions and tails from Utah and Wyoming uranium mills (1)[4] indicated that at least some clays and soils may have a significant absorption capacity for radium and other radionuclides (2). The present Bureau of Mines

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[4]Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

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investigation was initiated to obtain data on New Mexico soils and to develop a better understanding of the absorption capacity of soils adjacent to the tailing ponds for the radionuclides that are found in uranium processing tailing solutions. A second and future objective of the program is to determine how the absorption phenomena may be used for better tailing pond design and construction.

The following regulations and related information were used to develop and guide the exploratory experimental studies:

1. Environmental Protection Agency (EPA) regulations, which went into effect June 24, 1977, specify that the combined maximum concentration permitted for Ra-226 and Ra-228 in water supplies is 11.1 disintegrations per minute per liter, or 5 picocuries per liter (pCi/l) (8).

2. The most important radionuclide hazards associated with tailing pond solutions are Ra-226, Th-230, and Pb-210 (2, 7).

3. Literature shows that significant radionuclide concentrations do occur in solutions associated with uranium tailing ponds. The following radium concentrations have been reported: (a) alkaline tailing solution, 100 to 1,200 pCi/l; and (b) acid tailing solution, 2,800 to 28,000 pCi/l (4).

4. Monitor wells have shown diminishing or no radium present as the distance from tailing ponds increases (2). It is speculated that fixation or precipitation occurs in or near the tailing ponds.

5. Most of the radium in ores remains with the solids during leaching. Acid leaching dissolves up to 5 pct of the radium and up to 50 pct of the thorium from uranium ores. Alkaline leaching dissolves 2 to 3 pct of the radium and practically no thorium. The radium concentrations in acid leach tails solutions can be reduced as much as 98 pct by neutralizing to pH 8 or by treating with a small amount of soluble barium salt. The radium content of alkaline leach tails solutions can be reduced up to 90 pct by flocculating with ferrous sulfate. If the ferrous sulfate treatment is followed by barite treatment, additional radium is removed (4).

DESCRIPTION OF SAMPLES

Six soils and three tailing samples were obtained from the Grants, N. Mex., uranium milling areas. All solids were ground to pass a 10-mesh screen. Composition and analytical data on these samples are listed in table 1. Major constituents in all samples were quartz and feldspar. Total clays in the samples ranged from <2 to 5 pct. The concentrations of the major elements, plus radium, thorium, and uranium, are listed. The types of samples and depths from which they were obtained are also listed. The major clay types in samples 1 through 9 were montmorillonite and kaolinite. The radium, thorium, and uranium concentrations and the pH of the tailing pond liquors that were obtained are listed in table 2. Radium-226 in the samples ranged from 25 to 309 pCi/l, and thorium ranged from 0 to 440,000 pCi/l. The tailing solutions that had a pH of $\leq$1.5 contained significantly more thorium than the other solution samples.

TABLE 1. - Composition of the New Mexico solid samples used in absorption tests

Sample	Type of solid	Depth obtained	Radium, pCi/g	Thorium, pCi/g	Composition, wt-pct											
					U_3O_8	V_2O_5	Fe	Ca	CO_2	Mg	Organic C	$SO_4^=$	SiO_2	Al_2O_3	$S^=$	$P_2O_5^=$
1	Material added to bottom of tailing pond[1].	Surface...	2.8	9.1	0.0012	0.01	3.9	2.2	2.0	0.82	<0.01	0.08	59.6	22.1	0.02	0.21
2	Soil 1[1].	...do.....	1.7	1.2	.0009	.006	2.2	2.1	1.6	.76	.15	.04	76.2	15.1	.01	.24
3	Soil[1]...	14 feet...	3.4	.15	.0010	<.005	2.2	2.4	2.4	.71	1.3	.06	78.4	13.2	.01	2.0
4	Lava rock[2]	Surface...	1.0	.50	.0010	.02	8.8	7.0	.5	4.4	.12	.21	50.8	17.2	.01	<.04
5	Slime tail[3].	...do.....	220	92	.0106	.03	1.3	7.2	7.8	.17	<.1	.31	70.2	7.9	.21	.29
6	Soil 2[2].	...do.....	2.3	4.0	.0013	.005	1.5	.44	.1	.34	.4	.08	82.2	10.7	.01	.55
7	Sand and slime.[3]	...do.....	44	30	.0035	.02	1.3	2.2	<.1	.21	<.1	3.31	80.2	10.8	.09	<.03
		...do.....														
8	Soil 3[3].	...do.....	4.2	3.2	.0007	<.005	1.4	.18	<.1	.14	<.1	.06	88.2	8.9	<.01	.12
9	Soil[3]...	5 feet....	6.4	2.5	.0009	<.005	1.6	.44	<.1	.27	<.1	.04	85.2	9.4	<.01	.22

[1] 5 pct clay.
[2] Less than 2 pct clay.
[3] 2 to 5 pct clay.

TABLE 2. - Radium, thorium, and uranium concentrations and pH values for New Mexico tailing pond solutions used in absorption tests

Sample	Radium, pCi/l	Thorium, pCi/l	U_3O_8, g/l	pH
10.....	25	46,700	0.090	1.5
11.....	121	0	.135	10.1
12.....	309	440,000	.104	.9
13 (spiked).....	23,000	46,700	.090	1.5
14 (spiked).....	12,300	440,000	.104	.9

EXPERIMENTAL PROCEDURES

Laboratory Techniques

Batch contact tests were performed using tailing solutions and solid absorbents; the aqueous-to-solid ratios were 35:1 and 700:1. The ratios were chosen to provide convenient sample sizes for both the solid-solution contacting and the subsequent analytical determinations. The 35:1 ratio tests were made by stirring 10 g of each minus 10-mesh solid sample into 350 ml of the test solution in a 600-ml beaker. The tests were conducted at room temperature, and a propeller-type stirring device was used to agitate the mixture. For the 700:1 ratio tests, 0.5 g of the minus 10-mesh sample was added to the 350 ml of test solution. The resulting mixtures were filtered, and the radium and thorium concentrations in the filtrates were determined. Carrier-free Ra-226 was added to the No. 10 and 12 tailing solutions; these samples are numbered 13 and 14 (see table 2). This was done to increase the Ra-226:Ra-223-224 ratio to reduce the interference during analysis caused by Ra-223-224 (daughters of U-235 and Th-232, respectively). The extra radium in the spiked samples 13 and 14 did not affect the radium absorption results. This was probably due to the very large capacity that the solids had for absorbing radium. The thorium concentrations in the solution were used without alteration. The contact times of the solutions and solids ranged from 15 to 240 minutes depending on the absorption achieved during the tests. Test times were generally increased until radium removal efficiencies were 90 pct or were constant. If the radium removed was less than 70 pct during acid tailing tests in 60 minutes, the tests were discontinued. The radium and thorium in the filtrates were separated and determined with an alpha spectrometer. Soil samples that absorbed more than 70 pct of the radium from acid tailings were used for desorption testing. Also one sample that did not absorb radium to the above amounts was used to show how a weak absorber responded to absorption tests.

Analytical Techniques

The procedure used to recover the radium and thorium from solution is summarized as follows: Radium and thorium were coprecipitated with lead sulfate. The lead sulfate was dissolved in a strongly basic diethylenetriaminepentaacetic acid (DTPA) solution. If radium was to be determined, the solution was acidified to pH 4, and barium-radium sulfate was precipitated by adding barium chloride. The barium-radium sulfate was filtered on a membrane

filter giving a precipitate with an area of 10.75 cm^2. This area gives a thin precipitate, and greatly reduces self-absorption of the alpha particles. When determining thorium, the DTPA solution was contacted with bis(2-ethylhexyl) phosphoric acid (EHPA) to extract the thorium from the aqueous phase; then the thorium was stripped from the organic phase with an oxalic acid solution. The thorium was electrodeposited from the oxalic acid solution onto a stainless steel plate on which the deposited thorium covered an area of 1.77 cm^2. Both radium and thorium were then determined by measuring the activity of their alpha particle energies with an alpha spectrometer. Radium determinations made with the alpha spectrometer were checked routinely using the deemanation method developed by D. R. Rushing and others (6). This procedure is specific for Ra-226. Detailed procedures for the radium and thorium separations and determinations using alpha spectrometry are found in the appendix. The alpha spectrometer is shown in figure 1.

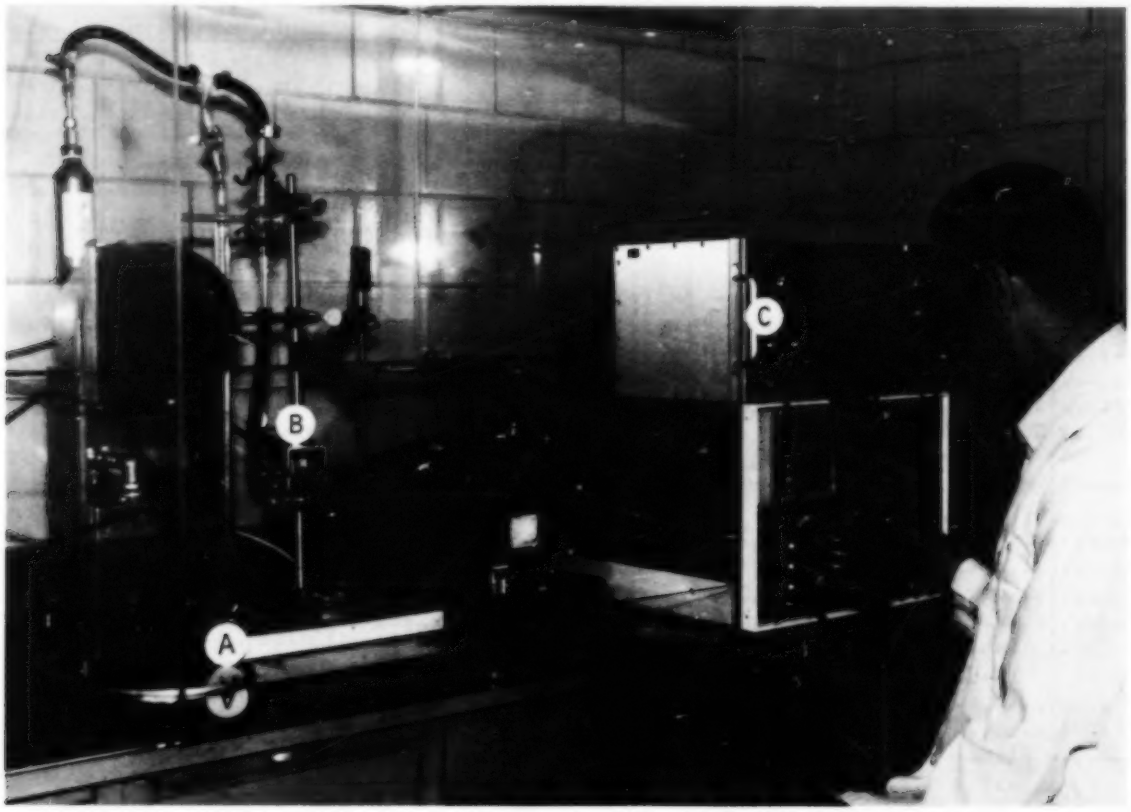

FIGURE 1. - Alpha spectrometer. A, Dual-vacuum chambers; B, pressure regulator; C, electronics and multichannel analyzer.

EXPERIMENTAL ABSORPTION STUDIES

Batch contact tests were run to evaluate the various possible combinations of solid samples and tailing solutions. Removal efficiencies of radium using 350 ml of tailing pond liquors and either 10 or 0.5 g of the soils or tailing solids (previously described in table 1) are shown in table 3. In this series of tests, tailing solutions were contacted with solids obtained from areas near the Grants, N. Mex., tailing ponds. Soil samples 2, 3, 4, and 9 are shown to have good absorption characteristics for radium even when the solution-to-solid ratio is 700:1. Most of the soil samples gave better removal of radium with increased contact time, whereas better thorium absorption was obtained in 1 hour than in 4 hours.

TABLE 3. - Removal efficiencies of radium and thorium using soils and tailing samples when contacted with tailing pond solution

Solid[1]	Type of solid	Solution[2]		Solution-to-solid ratio	Radium removed, pct, at contact time of--			Thorium removed, pct, at contact time of--		
		Radium, pCi/l	Thorium, pCi/l		15 min	60 min	240 min	15 min	60 min	240 min
1.....	Material added to bottom tailing pond.	121	0	35:1	NAp	81	78	NAp	NAp	NAp
1.....	...do....	23,000	46,700	35:1	NAp	23	NAp	0	0	NAp
1.....	...do....	12,300	440,000	35:1	NAp	3.1	NAp	NAp	0	NAp
2.....	Surface soil 1.	121	0	35:1	86	83	82	NAp	NAp	NAp
2.....	...do....	121	0	700:1	NAp	7.1	NAp	NAp	NAp	NAp
2.....	...do....	23,000	46,700	35:1	88	97	NAp	0	0	NAp
2.....	...do....	23,000	46,700	700:1	NAp	16	NAp	NAp	NAp	NAp
2.....	...do....	12,300	440,000	35:1	84	94	96	0	0	NAp
2.....	...do....	12,300	440,000	700:1	NAp	22	NAp	NAp	0	NAp
3.....	Soil, 14 feet deep.	121	0	35:1	86	88	86	NAp	NAp	NAp
3.....	...do....	121	0	700:1	NAp	25	NAp	NAp	NAp	NAp
3.....	...do....	23,000	46,700	35:1	67	87	96	13	0	0
3.....	...do....	23,000	46,700	700:1	NAp	1.6	NAp	NAp	0	NAp
3.....	...do....	12,300	440,000	35:1	60	25	80	0	0	0
3.....	...do....	12,300	440,000	700:1	NAp	16	NAp	NAp	0	NAp
4.....	Lava rock.	121	0	35:1	NAp	50	45	NAp	NAp	NAp
4.....	...do....	23,000	46,700	35:1	NAp	70	90	NAp	22	0
4.....	...do....	12,300	440,000	700:1	NAp	52	70	NAp	0	0
5.....	Slime tail.	121	0	35:1	NAp	4.9	NAp	NAp	NAp	NAp
5.....	...do....	23,000	46,700	35:1	NAp	0	NAp	NAp	32	NAp
5.....	...do....	12,300	440,000	35:1	NAp	51	NAp	NAp	0	NAp
6.....	Surface soil 2.	121	0	35:1	NAp	86	84	NAp	NAp	NAp
6.....	...do....	23,000	46,700	35:1	NAp	49	70	NAp	60	6.9
6.....	...do....	12,300	440,000	35:1	NAp	65	43	NAp	0	0
7.....	Sand and slime tail.	121	0	35:1	NAp	72	NAp	NAp	NAp	NAp

See footnotes at end of table.

TABLE 3. - Removal efficiencies of radium and thorium using soils and tailing samples when contacted with tailing pond solutions--Continued

Solid[1]	Type of solid	Solution[2]		Solution-to-solid ratio	Radium removed, pct, at contact time of--			Thorium removed, pct, at contact time of--		
		Radium, pCi/l	Thorium, pCi/l		15 min	60 min	240 min	15 min	60 min	240 min
7.....	...do....	23,000	46,700	35:1	NAp	47	NAp	NAp	14	NAp
7.....	...do....	12,300	440,000	35:1	NAp	45	NAp	NAp	0	NAp
8.....	Surface soil 3.	121	0	35:1	70	83	82	NAp	NAp	NAp
8.....	...do....	121	0	700:1	NAp	0	NAp	NAp	NAp	NAp
8.....	...do....	23,000	46,700	35:1	NAp	18	48	NAp	21	0
8.....	...do....	12,300	440,000	35:1	NAp	31	NAp	NAp	0	NAp
9.....	Soil, 5 feet deep.	121	0	35:1	80	81	84	NAp	NAp	NAp
9.....	...do....	121	0	700:1	NAp	25	NAp	NAp	NAp	NAp
9.....	...do....	23,000	46,700	35:1	48	78	96	0	48	9.5
9.....	...do....	23,000	46,700	700:1	NAp	0	NAp	NAp	0	NAp
9.....	...do....	12,300	440,000	35:1	67	79	91	20	23	32
9.....	...do....	12,300	440,000	700:1	NAp	67	NAp	NAp	0	NAp

NAp Not applicable.
[1] See table 1 for sample analysis.
[2] See table 2 for additional solution information.

SUPPLEMENTAL ABSORPTION STUDIES

Some milling operations in Colorado, New Mexico, and Utah use barium chloride to reduce the radium content of mining waste waters or processing waste waters. As a short supplement to this report, the following results were obtained using barium chloride at concentrations used at some milling operations.

Barium chloride was added to tailing solutions from six uranium mills. The barium concentrations were equivalent to 0.05 and 0.30 g/l. Radium removal efficiencies ranged from 25 to 99.98 percent. The pH and removal efficiencies are shown in table 4.

TABLE 4. - Radium removal efficiencies from tailing pond solutions by $BaCl_2$ additions

Tailing pond solution	pH	Radium removal, pct	
		0.05 g/l Ba^{++}	0.30 g/l Ba^{++}
Wyoming.....	0.5	98.4	98.7
Do.....	10.5	99.4	99.7
Southern Utah.....	3.5	64	68
Do.....	10.5	93	71
New Mexico.....	1.5	97	99.98
Do.....	10.1	25	87

EXPERIMENTAL DESORPTION STUDIES

A soil that absorbs but does not desorb radium would be best for tailing seepage control. Because they showed high absorption efficiencies, soil samples 2, 3, 4, and 9 were used for desorption tests. In order to determine desorption characteristics of these soils, they were loaded with 317, 308, 309, and 315 pCi/g of radium, respectively, and used in desorption tests. Sample 8 was also used as example of a weak absorber and was loaded with 312 pCi/g of radium. Solutions containing NaCl, NH_4Cl, $NaHCO_3$, and NH_4NO_3 in concentrations of 1 and 10 g/l were contacted with 10 g of the above solids for 1- and 4-hour durations. The solution volume was 350 ml. These desorbing solutions contain the type of ions that can be introduced by changes or modifications in the uranium operations, and the tests were designed to investigate the effect of these new ions on the previously absorbed radium. The results of these tests are summarized in table 5. Samples are grouped according to the desorbing solutions used. Desorptions ranged from 0 to 75 pct. The surface soil (sample 2) showed the least overall desorption. NH_4NO_3 and NH_4Cl desorbed more radium from the solids than NaCl or $NaHCO_3$. Higher concentration of salts gave high desorption values for all salts. Increasing the contact time sometimes gave less desorption and sometimes more leading to no set pattern with respect to contact time. Sample 8, which was a weak absorber for radium, showed the most desorption of radium.

TABLE 5. - Desorption studies on 10 g of selected samples

Sample[1]	Contact time, min	Radium desorbed with 350 ml of solution, pct							
		NH_4NO_3		$NaHCO_3$		NH_4Cl		NaCl	
		1 g/l	10 g/l	1 g/l	10 g/l	1 g/l	10 g/l	1 g/l	10 g/l
2.....	60	0.89	8.20	0.10	0.28	2.4	6.94	0.38	4.3
	240	.58	5.84	.10	.11	.88	6.97	.38	3.6
3.....	60	3.21	27.7	.88	0	5.42	35.6	1.7	13.4
	240	.88	15.2	0	0	11.8	26.9	.26	7.3
4.....	60	12.0	61.9	0	2.16	19.9	69.1	6.5	45.9
	240	7.24	55.4	0	0	13.6	69.3	.84	34.3
8.....	60	43.6	64.7	0	4.46	33.0	50.6	8.7	40.5
	240	43.8	75.1	0	4.55	53.9	51.0	8.3	45.2
9.....	60	17.8	57.7	0	1.36	20.2	66.6	6.8	38.0
	240	11.6	50.6	0	1.55	16.1	67.9	4.4	45.0

[1]Sample 2 is soil from the surface, 317 pCi/g Ra.
Sample 3 is soil 14 feet deep, 308 pCi/g Ra.
Sample 4 is lava rock, 309 pCi/g Ra.
Sample 8 is surface soil, 312 pCi/g Ra.
Sample 9 is soil 5 feet deep, 315 pCi/g Ra.

DISCUSSION, CONCLUSIONS, AND RECOMMENDATIONS

The absorption and desorption of radium and thorium from tailing liquors by clay and other materials were investigated. The following summarizes the principal observations and results from the batch contact experiments in this study:

- At high solution-to-solid ratios radium absorption ranged from 0 to 97 pct.
- Absorption of thorium varied between 0 and approximately 60 pct.
- Essentially all of the New Mexico samples absorbed some radium from the acidic tailing solutions, but the thorium absorption was nil in most cases.
- Batch desorption tests using relatively dilute ammonium and sodium salt solutions showed desorptions ranging from essentially 0 to 75 pct.
- The order of desorption effectiveness for the salts was $NH_4Cl = NH_4NO_3 > NaCl > NaHCO_3$.

The test results and observations have led to the following tentative conclusions:

1. Soils, clays, and other materials can absorb large amounts of radium from uranium tailing solutions, but it has not been possible to relate the absorption to specific chemical or physical characteristics. Relationships do appear to exist, but based on the presently available information, the absorption capacity of each material must be determined experimentally.

2. Thorium was absorbed only slightly by the soil samples tested.

3. The absorbed radium can be desorbed from some materials by relatively dilute salt solutions. The soils with the best absorption characteristics were the most resistant to desorption.

The initial radium absorption results are encouraging, but additional information will be needed to determine if the procedure can be effectively used to improve uranium tailing pond design and management. The following additional work is recommended:

1. Further studies should be conducted to determine if specific ralationships between the soil composition and the radium absorption capacity can be established. These investigations should include tests on both solids and tailing solution samples from other areas, and additional mineralogical and other identification techniques should be used.

2. Chromatographic-type absorption tests to investigate the long-range stability of the radium absorption should also be considered. These tests may require relatively large volumes of tailing solution and probably should be conducted at operating mill sites.

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APPENDIX.--ANALYTICAL PROCEDURES

The quantitative isolation of radium by precipitation and the separation of thorium by solvent extraction and electrodeposition can be achieved by the following procedures. The radium and thorium concentrations can then be determined by alpha spectrometry. Well-resolved alpha spectra result from an electroplated thorium sample and an extremely small barium-radium precipitate (0.75 mg) spread uniformly over their respective areas.

Instrumentation

Alpha energy spectra were obtained with a Tracor-Northern 1710,[1] 4096-channel analyzer with one input for each 1,024 channels. The analyzer was connected to Ortec 450-mm^2 ruggedized surface barrier detectors, Ortec Model 121 preamplifiers, an Ortec Model 428 detector bias supply, and Ortec Model 485 amplifiers. Samples were counted in vacuum chambers designed by the Bureau of Mines and the data printed by a Texas Instruments 700 ASR printer.

The analyzer was calibrated with a New England Nuclear 52 nCi Am-241 source and adjusted to give 10 kev per channel energy spectra. The first 100 channels of each 1,024-channel energy set were blocked out with a low-energy discriminator to eliminate noise from the detector and electronics.

Reagents

H_2SO_4 - concentrated 1 pct, and 5 pct

HCl - concentrated

K_2SO_4

$Pb(NO_3)_2$ - 3.2 pct

Solution for lead sulfate wash - 25 g K_2SO_4 dissolved in 1 liter of 1 pct H_2SO_4.

DTPA (diethylenetriaminepentaacetic acid) - 0.17 M - dissolve 67 g of DTPA and 32 g of NaOH in 400 ml of water. Filter through two glass fiber filters, dilute to 1 liter, and adjust pH to 10 with NaOH or $HClO_4$.

Na_2SO_4 - 20 pct

Acetic acid - 6 M

$BaCl_2$ - dissolve 0.4 g of $BaCl_2.2H_2O$ per liter of water

HNO_3 - concentrated and 4 M

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[1]Reference to specific trade names does not imply endorsement by the Bureau of Mines.

$Al(NO_3)_3$ - 2 M - dissolve 750 g of $Al(NO_3)_2 \cdot 9H_2O$ in 450 ml of H_2O and 50 ml of concentrated HNO_3. Filter through two glass fiber filters and dilute to 1 liter. Extract the entire solution for 1 minute with 100 ml of 15 pct EHPA. Discard organic and repeat extraction. Wash the aqueous solution with two 100-ml portions of chloroform and with one 100-ml portions of n-heptane.

EHPA - bis(2-ethylhexyl) phosphoric acid - 5 pct and 15 pct - wash 1 liter of 15 pct EHPA in n-heptane for 1 minute with a 200-ml portion of 1:1 solution of 2 M diammonium citrate and concentrated HNO_3 and twice with 200-ml portions of 4 M HNO_3. Dilute 300-ml of solution to 900 ml with n-heptane and wash twice with 200-ml portions of 4 M HNO_3.

H_2O_2 - 30 pct

Toluene

Oxalic acid - 0.4 M

Ammonium DTPA - 1 M

NH_4Cl - saturated

NH_4OH - concentrated and 0.1 M

HF - 1:5 solution of 48 pct HF

Radium and Thorium Separation and Determination

The following chemical procedure for separating and analyzing radium and thorium in solution was adapted from a procedure published by D. R. Percival and D. B. Martin (5).[2]

Take 300 ml of the sample solution in a 600-ml beaker and add 20 ml concentrated H_2SO_4, 4 ml of concentrated HCl, and 25 g of K_2SO_4. Bring this solution to a boil and add a 5-ml portion of 3.2 pct $Pb(NO_3)_2$ solution over a 20-second interval while stirring. Boil for 3 minutes and add a second 5-ml portion of the $Pb(NO_3)_2$ solution. Boil for another 2 minutes. Cool the sample in a cold-water bath.

After cooling, centrifuge the sample and decant and discard the supernatant liquor. Wash the precipitate with 20 ml of lead sulfate wash solution. The precipitate contains all the radium and thorium that was in the sample initially.

Radium

To the precipitate add 7.5 ml of DTPA with stirring to dissolve the $PbSO_4$ precipitate and transfer the solution to a 40-ml centrifuge tube using another 7.5 ml of DTPA and then H_2O for a quantitative transfer. The final volume should be about 25 ml. Place in a 90° C water bath and add 1 ml of 20 pct Na_2SO_4 and 2 ml of 6 M acetic acid. The pH will now be 4. Add three 1-ml portions of $BaCl_2$ slowly to the hot solution allowing about 1 minute between each addition. Digest the precipitate in the water bath for 7 minutes and then cool the sample for 5 minutes in a cold water bath. Add 4 drops of $BaCl_2$ to scavenge any remaining radium. Cool for another 5 minutes and centrifuge for 8 minutes. After centrifuging, filter on a Millipore HABP 04700 membrane filter using 0.5 pct H_2SO_4 to disperse and wash the precipitate from the centrifuge tube. Mount the filter on a stainless steel plate covered with double-stick tape and dry under a heat lamp. Do not let filter get so hot that it will start to curl and will not lie flat. The mounted filter is now ready for alpha spectrometry.

Thorium

To determine thorium dissolve the $PbSO_4$ precipitate in 15 ml of DTPA. Transfer the resulting solution to a separatory funnel containing 40 ml of H_2O. The volume after the transfer will be about 60 ml. Add 20 ml of concentrated HNO_3, 10 ml of 2 M $Al(NO_3)_3$, and 1 ml of 30 pct H_2O_2. Shake the separatory funnel to insure mixing and let stand for 10 minutes. Add 10 ml of 5 pct EHPA and contact the phases vigorously for 15 minutes. Allow 7 minutes for phase separation and discard the aqueous phase. Add 10 ml of 4 M HNO_3 and 0.5 ml of 30 pct H_2O_2 and mix for 1 minute. Again, allow the phases to separate and discard the aqueous phase. Wash with another 10 ml of 4 M HNO_3. Discard

[2] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

the aqueous phase. Add 10 ml of toluene and 4.5 ml of 0.4 M oxalic acid and shake vigorously for 2 minutes. Allow 5 minutes for phase separation and transfer the aqueous phase to a 40-ml centrifuge tube. To the organic phase in the separating funnel add another 4.5 ml of 0.4 M oxalic acid and shake for 2 minutes. Allow 10 minutes for phase separation, withdraw the aqueous phase and add it to the centrifuge tube. Discard the organic phase.

Add 3 drops of 1 M ammonium DTPA and 1.5 ml of saturated NH_4Cl, and 1 drop of methyl red indicator. Add concentrated NH_4OH to the yellow end point and then add 6 drops extra. Add concentrated HCl until the red reappears. Add 3 drops of 1:5 HF.

Transfer the solution to an electrodeposition cell and place the platinum anode 4 mm above the stainless steel deposition plate. Electrodeposit the thorium using a 0.80 amp/cm^2 current density for 50 minutes. The electrodeposition cell should be cooled with cold water so that solution temperature does not rise above 50° C. At the end of electrodeposition, add 2 ml of concentrated NH_4OH, stop the stirrer, and lower the cell away from the anode. Wash the stainless steel deposition plate with 0.1 M HN_4OH and heat on a high-temperature hotplate for 5 minutes. The specimen is ready for spectrometry. If the specimen contains more than 30 μg of Th-232, it will have to be rerun using a smaller sample.

Counting Procedure

The flat plates were counted in a vacuum of 4 mm, at a 1-inch source distance from the detector (or 2 mm pressure for a 2-inch distance) to stop the recoil atoms. A negative potential was also applied to the counting plate to collect the recoil atoms emitted from the plate (4). This prevents contamination of the alpha detector. The efficiency of the counting system was obtained by using a National Bureau of Standards SRM-4953-B radium source in the above separation procedure. Samples were counted for a time sufficient to give good counting statistics (3 pct error at the 95-pct confidence level). Radium and thorium concentrations were computed from the gross areas under their photopeaks. Background under these peaks were less than 0.5 count per hour.

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